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(54) **A process and an apparatus for producing a thin photoimageable coating on a metallic-layered substrate.**

(57) A process for producing thin photoresists on printed circuit boards wherein a metallic-layered substrate is conveyed beneath a free falling curtain of a photopolymerizable substance, said substance having a viscosity of 30-120 seconds DIN cup 4 at 25°C, corresponding to 104-608 mPas, and being applied at a curtain height of 5 - 25 cm above the board to form a coating having a dry film thickness less than or equal 25 µm after the coated surfaces are dried, whereupon the surfaces are available for photoimaging, developing, etching and stripping operations. The apparatus for producing such thin photoimageable coatings on metallic-layered substrates comprises vacuum means to maintain the boards on the conveyance means in a flat fixed position as they pass beneath the curtain. According to another aspect of the invention the apparatus also comprises a cooling means for cooling the boards from underneath while their upper side is being dryed subsequent to coating in the coating station.

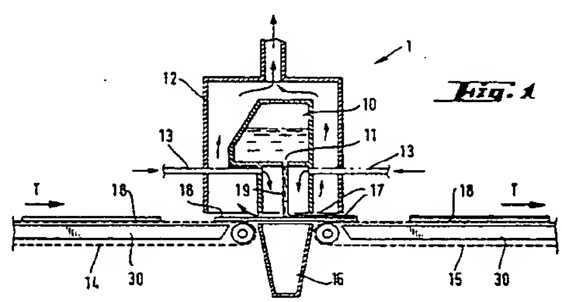

Fig. 1

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The invention relates to a process for producing a thin photoimageable coating on a metallic-layered substrate according to the preamble of claim 1. The invention also relates to a respective coating apparatus according to the preamble of claim 13.

In the manufacture of printed circuit boards, a photoresist is used to transfer the outline of the circuit into the copper surface of the board. The name photoresist defines the dual functioning nature of this material. First it is a photopolymer whose chemical properties are changed by exposure to ultraviolet radiation. That exposure is done selectively through a mask outlining the circuit being defined. The dual functioning comes into play after developing the photopolymer, where the soft unwanted areas are washed off the copper surface. What remains is a protective covering of hardened polymer only in those areas outlined by the exposure mask. In one application this protective covering resists the etching process so that only the copper left unprotected is etched away. When the resist is finally removed, the protected copper circuit lines underneath become the electrical conductors of the circuit board.

One real measure of the evolution of printed circuit board technology is the width of the copper circuit lines and the spacing between them. As the component density and circuits per square inch increase, the width of the circuit lines and the spaces between them must decrease. The current state of the art is about 250 µm lines with about 250 µm spaces. This geometry is ultimately determined by the process technology that allows the reliable fabrication of circuit boards within tolerances acceptable to the industry. In normal production a 250 µm wide circuit line can be controlled to within plus or minus 25 µm. If this line is spaced 250 µm from an adjacent line that may also vary by only 1 mil, there is little chance of having broken lines or short circuiting between lines. If, however, that line spacing geometry is reduced to 25 µm lines and spaces and less, the previous tolerance is unacceptable and the process technology must be advanced to achieve and maintain a tighter tolerance.

Two methods are commonly used for applying photoresist to the copper surface of a circuit board. One of these is coating and the other is lamination. In coating, a fluid containing the photopolymer dissolved in solvent is applied to the copper surface in a thin uniform layer. The solvent is evaporated away and a uniform film of photoresist is deposited onto the copper surface. In lamination, a previously coated and dried film of photoresist on a carrier web is bonded to the copper surface using heat and pressure, after which the carrier web is stripped away.

Most of the circuit boards produced today use the dry film method for two primary reasons. First there is no solvent fluid to cause safety, personnel, environmental or disposal problems. Secondly, there is no liquid photoresist to get inside the drill-through holes to contaminate them and jeopardize the integrity of the plated through connections. These two advantages of dry film over coating are substantial but they are obtained at a price. One price is economic as dry film is about three times as costly per square foot as a coated photoresist. Additionally, dry film is a wasteful process, with the resist overhanging the board edges, for example, being totally useless. Dry film also requires the maintenance of substantial and varied inventories in order to cover the various etching and plating operations. Dry films are also susceptible to loss of resolution through overexposure and etchant leaching beneath the resist.

The other price, far more costly, is technological. Dry film has not been produced reliably below a thickness of one mil. In order to reduce the line spacing geometry so that circuit density can be significantly increased, it is necessary to reduce the thickness of the photoresist to a range of about 2,5 µm to about 5,0 µm.

Accordingly, as the demand for finer resolution has grown, greater consideration has been given to liquid photoimageable primary resists. The available application techniques for such liquids have also, however, exhibited certain disadvantages. Spin coating is laborious and does not allow for high volume coating. Dip coating does not assure even coating thicknesses. Roller coating is a slower process which must accommodate potential contamination of the rollers. Electrostatic spray coating involves a more complex approach with the potential for waste of the photoresist spray. Finally, electrocoating requires the application of plating technology with its greater complexity, higher cost and required close bath monitoring.

Curtain coating approaches wherein the circuit boards are conveyed beneath a curtain of photoresist have been successfully adopted for use in producing solder masks on printed circuit boards. Such a curtain coating approach and the applicable parameters have been described in U.S. 4,230,793. However, in view of the need to apply very thin coatings on thin inner layer core and to coat the second side of the board without damaging the first coated side, curtain coating has not been suggested for primary photoimaging. In fact, it has been suggested that only minimum deposited film thicknesses of about 50 microns can be achieved while still retaining a stable resin curtain. [see ZEV-Leiterplatten, pp. 20-24 (11/90)]. Alternatively, somewhat thinner film deposition requires rapid board transport beneath the curtain and/or substantial viscosity reduction, neither approach ensuring proper deposition and/or curtain stability.

An article by Dr. N. Ivory in PC Fab. pp. 30-38 (April 1990) also suggests the possibility of the curtain coating approach for primary imaging of circuit boards. This discussion, however, makes reference to the above noted undesirable viscosity reduction

and increased substrate feed rate in order to utilize such a technique. Two additional problems are identified. Thus, difficulties are noted in coating thin innerlayer laminates due to bending and buckling phenomena. Carrier frames are therefore required in such circumstances. Protection from etchant attack of the plated through holes in double-sided and multilayer boards is also a problem whose solution requires costly additional processing.

It has now been surprisingly discovered that by selection of identified process variables, a curtain coating process can be readily and efficiently utilized for the primary imaging of printed circuit boards. Identification of appropriate lacquer viscosities, curtain height and board speed beneath the curtain combined with maintenance of the board on the conveyance means in a flat, fixed position as it passes beneath the curtain substantially eliminate the prior art difficulties while also eliminating the need for extraneous equipment such as the carrier frame and extraneous operations such as the hole protection. More specifically, the process allows for the deposition of the requisite thin films (less than about 38 μm dry thickness) for the primary imaging operation. Excellent adhesion on the copper substrate; greater flexibility in the operating conditions, i.e. variation available to meet specific circumstances; high resolution capabilities at 75-125 μm lines and spaces and perhaps even finer lines and spaces; straight, well-defined side walls after development; good chemical resistance of the coating in cupric chloride and ammoniacal etching systems; are all benefits achieved with the instant process.

According to the invention, a liquid substance is applied as a flowing curtain to a metallic-coated substrate conveyed in a fixed position through the curtain, said liquid substance having a viscosity of 30-120 seconds din CUP 4 at 25°C, corresponding to 104-608 mPas, and being applied at a curtain height of from 5-25 cm above the substrate, the coated substrate is conveyed to a drying zone to form a coating having a maximum wet film thickness of about 25 μm to about 38 μm, corresponding to a dry film thickness of less than about 25 μm on a metallic-covered substrate. If desired the process can be repeated to coat the second side of the substrate. The apparatus for producing such thin photoimageable coatings on metallic-layered substrates comprises vacuum means to maintain the boards on the conveyance means in a flat fixed position as they pass beneath the curtain. According to another aspect of the invention the apparatus also comprises a cooling means for cooling the boards from underneath while their upper side is being dryed subsequent to coating in the coating station. Preferred embodiments and other features of the invention will now be described in greater detail with reference to the accompanying schematic drawings wherein:

Fig. 1 is a view of a coating station of a coating apparatus for performing the process in accordance with the invention,

Fig. 2 is a more detailed view of the conveying means in the coating station,

Fig. 3 is a view of an accompanying drying oven, and

Fig. 4 is a detailed view of the cooling means in the drying oven.

An apparatus for for producing a thin photoimageable coating on a metal-layered substrate comprises at least one coating station 1 and at least one drying oven 2. Entry and exit stations for substrates 18 to be coated are usually arranged apstream or downstream the coating station 1 respectively. For the sake of clearity of the figures they are not shown. The coating station 1 depicted in Fig. 1 comprises a coating head tank 10 in which there is a coating slot 11, an exhaust hood 12 for vapor control, inlet 13 for introduction of inert gas such as nitrogen when operating under such an atmosphere, conveyor means 14 and 15, trough 16 and gap 17, i.e. the distance between enclosed coating head 10 and the substrates passing thereunder. Delivery lines, pumps and the belt driving means are not shown.

The substrates 18 are moved into the direction indicated by arrow T by the conveyor means 14 and 15 below tank 10. A coating resin composition issuing from slot 11 drops in the form of a substantially free falling curtain 19 onto substrates 18 and forms a thin coating (≦ 25 μm dry film thickness) thereon. The viscosity, curtain height and the conveyance velocity can be related to one another, as discussed hereinafter, to produce an ideal photoimageable coating.

Fig. 2 shows one exemplary embodiment of the conveying means in the coating station 1. According to the depiction the conveying means 14 comprises an endless belt with perforations 35. The perforated belt is arranged in close ralationship to and directly above a metal platen 31 which comprises perforations 34. The perforated conveyor belt 14 is moveable relative to the metal plate 32. The metal plate 31 is part of a vacuum chuck 30 which is connected by a pump line 32 with a vacuum pump 33 or the like. By activation of the pump 33 a negative pressure p_2 is created iside the chuck 30 which is lower than the outside pressure p_1. Thus through the perforations 34 of the metal plate 31 of the chuck 30 and the perforations 35 of the perforated conveyor belt 14 the substrate 18, usually a circuit board to be coated, is sucked against the conveyor belt 14 and secured against slippage. It is to be understood that an equivalent set-up is chosen for the second belt conveyor 15 of the coating station.

Thus, in order to insure that the boards 18 are transferred through the curtain without significant movement or slippage, belts 14 and 15 are provided with means for fixedly transporting the boards. According to a preferred embodiment, as described with

reference to Fig. 2, vacuum means are preferably utilized wherein belts 14 and 15 are perforated and vacuum is applied therethrough to maintain the board. The fixed arrangement also insures that each board reaches the same acceleration speed, thereby providing for coating uniformity and repeatability. Other means such, for example, as traction devices or the use of belts composed of acrylonitrile/butadiene rubber, antistatic polytetrafluoroethylene, and the like, which grip the boards in transit, provide the same desired effect.

It is also preferable that trough 16 exhibits a slim design such that the space between conveyor belts 14 and 15 is minimized, i.e. preferably between 5 to 12 cm and most preferably about 9.0 cm. The limited gap further insures a smooth transition through the curtain. The thin trough design also provides for a more stable lower portion of the curtain and for reduced air entrapment in the recycled resist.

In terms of applicable process parameters, the appopriate relationship between lacquer viscosity, curtain height and bolt speed allows for the ready application of uniform thin films of from about 5 µm to about 38 µm dry thickness; preferably about 10 µm - 25 µm, and most preferably about 15 µm for the instant photoimageable application. Lacquer viscosities range from about 30-120 sec. DIN cup 4 at 25°C, corresponding to 104-108 mPas, preferably 45-70 sec., corresponding to 188-328 mPas, and most preferably 60 sec, corresponding to 272 mPas. Curtain heights vary from about 5-25 cm and are preferably 14 cm. Belt acceleration speeds range from 60-125 m/min, preferably 75-110 m/min and most preferably 90 m/min. It is to be noted that the construction of the unit eliminates the criticality of careful monitoring of the gap opening to achieve appropriate coating thickness.

The substrates to be coated are known to those skilled in the art and generally consist of epoxy resin or bismaleimide resin/fiber impregnated laminate constructions. The most prevalent core consists of a copper metal layer adhered to each side of an epoxy/glass base having about 125 µm thickness. The board dimensions may vary, with modification of the process parameters as required.

A wide variety of lacquer systems may be utilized in the instant process. Such systems will generally comprise a photopolymerizable resin component, a solvent or diluent, a photoinitiator activatable by actinic radiation and fillers, crosslinking agents, and the like, as needed. Typical resins include photosensitive epoxide resins having free curable epoxide groups. The photosensitive group is preferably an ethylenically unsaturated group such as an acrylic or methacrylic group. Such resins are disclosed, for example, in U.S. 3,989,610, 4,064,287, 4,108,803, 4,413,052, 4,390,615, among others, with these patents being fully incorporated herein. The epoxide resin can be based on bisphenols, novolacs, hydantoins, uracils and isocyanurates.

Photopolymerization initiators are also known to those skilled in the art and include benzoin ethers, anthraquinone derivatives, onium salts and metallocene complexes. Typical solvents include carboxylic acid esters of lower alcohols, dialkyl ethers, ketones and preferably hydroxyalkyl ethers. Additional photopolymerizable materials may also be present such as esters of alcohols with ethylenically unsaturated carboxylic acids. The coating composition can contain further customary additives such as fillers, dyes, pigments, levelling agents, flame retardants, photosensitizers, curing agents and curing accelerators. Solids content of the lacquer will generally range from about 30% to about 100%, by weight, and preferably 40% by weight.

Optional steps which may be conducted prior to lacquer application include precleaning of the inner layer core and filtration of the liquid photoresist. Precleaning may be conducted by physical means as by pumice scrubbing or by chemical approaches. Such cleaning eliminates contaminants and increases the degree of adhesion of the photoresist to the copper surface. Correspondingly, filtration of the liquid photoresist prior to introduction into the coater head minimizes the adverse impact of dust and gel particles during the residence period of the liquid in the coater.

The representative drying oven 2 depicted in Fig. 3 comprises continuing conveyor belt 23, heating elements 21 such as infrared rods and space 22 which allows for laminar air flow A over the coated substrates and for stabilization of the heat profile. For purposes of the instant invention, infrared heating has proven to provide a superior method of drying the thin coating in a fast and efficient manner. The infrared heat combined with modest airflow insures sufficient air movement over the coated boards and stabilizes the heat profile.

According to Fig. 4 the conveyor belt 23 rides on a metal support plate 20 and transports the coated boards to be dried into the direction indicated by the arrow T through the drying oven. Underneath the support plate 20 there is arranged a system of interconnected tubes 24. The tubes are connected through lines 25 with a reservoir 26 for a coolant C. As depicted in Fig. 4 a pump 27 serves for the transport of the coolant. A heat exchanger 28 can be arranged in the flux of the coolant C. Preferably water is used as the coolant C. By having the conveyor belt utilized in the drying zone ride on the cooled metal support plate a low temperature on the bottom surface of the board, i.e. the surface in contact with the belt, is ensured. This factor is of particular value during second side coating and drying in order to protect the first coated side which rides face down on the conveyor plate. Typical drying temperatures range from 80 to 150°C and typical conveyor speeds from about 4.0 to about

9.0 m/min. Current output, the length of the heating zone and the number of infrared rods will be selected on the basis of the oven type, the other process variables and maximum productivity. Current output will generally be greater for first side drying.

The imaging, developing, etching and stripping operations applicable to the coated boards are well known to those skilled in the art. Although negative resist technology is most applicable to such primary imaging, positive resists may be used. The latter are, however, particularly applicable for other coating applications. Negative resists function by photopolymerizing the areas of resist which will define the circuit during etching. The pattern is thus less soluble in the developer solution than the surrounding unexposed resist. Correspondingly, positive resists rely on a polymer which is rendered soluble in the appropriate developer upon exposure such that the unexposed areas of the resist define the circuit. In either approach, the polymer is stripped after etching.

In both the photopolymerizing and the subsequent photocrosslinking stage of the process of this invention actinic radiation of wavelength 200-600 nm is preferably used. Suitable sources of actinic radiation include carbon arcs, mercury vapour arcs, fluorescent lamps with phosphors emitting ultraviolet light, argon and xenon glow lamps, tungsten lamps, and photographic flood lamps. Of these, mercury vapour arcs, particularly sun lamps, fluorescent sun lamps, and metal halide lamps are most suitable. The times required for the exposures of the photopolymerizable composition and the still photocrosslinkable composition will depend upon a variety of factors which include, for example, the individual compounds used, the type of light source, and the distance of that source from the irradiated composition. Suitable times may be readily determined by those familiar with photopolymerization techniques. Optimum exposure energy ranges from 330 to 450 mJ/cm^2, with the optimum exposure times ranging from 5 to 20 seconds.

For the primary negative resists, the unexposed non-image areas may be removed by the use of aqueous alkaline solutions. Typical alkaline components include sodium and potassium carbonate, triethanolamine, monoethanolamine, anhydrous sodium sulfite, imidazolines, and the like.

Metal may be etched to form the printed circuit by means of etching fluids such as cupric chloride, ferric chloride and ammoniacal fluids such as ammonium persulfate solutions. After etching, the resist can be removed, i.e. stripped, with caustic solutions based, for example, on monoethanolamine or sodium hydroxide.

As previously noted, the curtain coating process of the invention provides a significant number of distinct advantages. In summary, it allows for the application of thin, uniform coatings necessary for primary imaging, for the use of thin inner layer core material and for excellent resolution in the imaged patterns to perhaps as small as 25 µm lines and spaces and less.

Although the primary focus of this descriptive material has been placed on coatings for primary imaging applications, it is to be noted that the process is equally applicable to printing plate, photochemical machining, photolithography applications, and the like. It is also to be noted that the process is applicable to liquid laser imageable photoresist technology wherein direct printing on the coating is achieved by means of laser techniques.

By way of a specific illustration of the process of the invention, a pre-filtered, epoxy/acrylate lacquer composition in propylene glycol methyl ether acetate solvent to a solids content of 40%, by weight, and having a viscosity of 60 seconds DIN cup 4 at 25°C, corresponding to 272 mPas, is introduced into the coating unit depicted in Fig. 1. The substrate is a pumice cleaned, 45 cm x 60 cm x 125 µm thick core of copper metal on epoxy glass with the 60 cm edge being the leading edge in terms of entering the curtain. The curtain height is 14 cm above the belts which are constructed to include a vacuum hold-down mechanism and which are set to run at 90 m/min. Seventeen boards are thus coated to provide a coating thickness thereon of 15 µm (dry film thickness).

The coated boards are transported into the drying zone on a conveyor belt composed of antistatic polytetrafluoroethylene over a cool metal plate, the drying zone having a infrared region of 2.1 meters featuring 18 infrared rods. The conveyor speed is set at 1.5 m/min with the constant current output for the infrared rods being 15 amperes. When the coating procedure is repeated on the second side of the board and the boards are returned to the drying zone, the current output for the infrared rods is 7.5 amperes. Boards with superior, uniform coatings are obtained.

The boards are then exposed through a high density art work having 125 µm lines and spaces utilizing mercury lamps having their major wavelength peak between 330-390 nm, with exposure energy at 150 mJ/cm^2. The boards are developed utilizing an aqueous potassium carbonate solution, etched with cupric chloride and then stripped utilizing a 15%, by weight, caustic solution.

Panel yield for the 17 boards and 34 images is 100%, i.e. each board exhibits defect free surfaces. Investigation of the etched surfaces reveals well defined, consistent 125 µm lines and spaces with exceptionally straight side walls in the etched indentations.

Summarizing, it is seen that this invention provides a novel curtain coating process for use in the primary imaging of printed circuit boards. Variations may be made in procedures and materials without departing from the scope of the invention as defined by the following claims.

Claims

1. A process for producing a thin photoimageable coating on a metallic-layered substrate comprising the steps of conveying said substrate in a fixed position on conveyance means beneath a free falling curtain of a photopolymerizable liquid having a viscosity of 30-120 seconds DIN cup 4 at 25°C, corresponding to 104-608 mPas, said curtain extending 5-25 cm above the substrate and the substrate passing beneath the curtain at a speed of about 60-125 m/min, thus forming a coating having a wet film thickness from about 25 µm to about 38 µm; and drying the coated substrate to form a photoimageable coating having a dry film thickness less than or equal 25 µm.

2. A process according to claim 1, wherein said metallic-covered substrate contains a sheet of copper metal on each side thereof.

3. A process according to claim 1 or 2, wherein said photopolymerizable liquid contains an epoxide resin having free curable epoxide groups and ethylenically unsaturated groups.

4. A process according to any one of the preceeding claims, wherein said viscosity ranges from 45-70 seconds DIN cup 4 at 25°C, corresponding to 188-328 mPas.

5. A process according to any one of the preceeding claims, wherein said conveyance means comprise a conveyance belt which is driven with a speed in the range from 75-110 m/min.

6. A process any one of the preceeding claims, wherein said fixed position is obtained by utilizing perforated conveyance means and applying a vacuum through said perforations to retain said substrate.

7. A process according to any one of the preceeding claims, wherein said fixed position is obtained by utilizing conveyance means with a grip inducing surface.

8. A process according to any one of the preceeding claims, wherein said viscosity is 60 seconds DIN cup 4 at 25°C, corresponding to 272 mPas, said curtain height is 14 cm and said belt speed is 90 m/min.

9. A process according to any one of the preceeding claims, wherein drying is obtained by applying infrared heating to said coated substrate.

10. A process according to claim 9, wherein said substrate is simultaneously cooled on the opposite side from underneath.

11. A process according to any one of the preceeding claims, wherein said photopolymerizable liquid is filtered before application to the substrate.

12. A process according to any one of the preceeding claims which is conducted on each surface of the substrate.

13. An apparatus for producing a thin photoimageable coating on a metallic-layered substrate (18) comprising at least one coating station (1) and one drying oven (2) and conveyance means (14, 15, 23) for transporting said substrate (18) through said coating station (1) and through said drying oven (2), wherein said said conveyance means (14, 15) in said coating station (1) comprises a vacuum means for applying a vacuum to said substrate (18) as it is transported beneath a free falling curtain (19) of photoplimerizable liquid.

14. An apparatus according to claim 13, wherein said conveyance means (14, 15) comprise a perforated belt, wherein said vacuum means comprise a perforated metal plate (31) which is part of a vacuum chuck (30), which in turn is connected with a vacuum pump (33) or the like, and wherein said perforated belt is arranged immediately above said vacuum plate (31) and is moveable relative to it.

15. An apparatus according to claim 13 or 14, wherein said drying oven (2) comprises means (21) to apply an infrared radiation to the coated upper surface of the substrate (18).

16. An apparatus according to any one of claims 13 to 15, wherein said drying oven (2) comprises cooling means which are arranged underneath said conveyance means for said substrate.

17. An apparatus according to claim 16, wherein said conveyance means are arranged in close relationship to and above a metal support plate (20) and wherein said cooling means comprise a system of interconnected tubes (24) which are arranged underneath said support plate (20) and which are connected with a reservoir (26) for a coolant (C).

18. An apparatus according to claim 17, wherein said coolant (C) is water.

19. An apparatus according to any one of claims 16 to 18, wherein the surface of said conveyance

means (23) supporting said substrate (18) in the drying oven (2) is coated with TEFLON®.

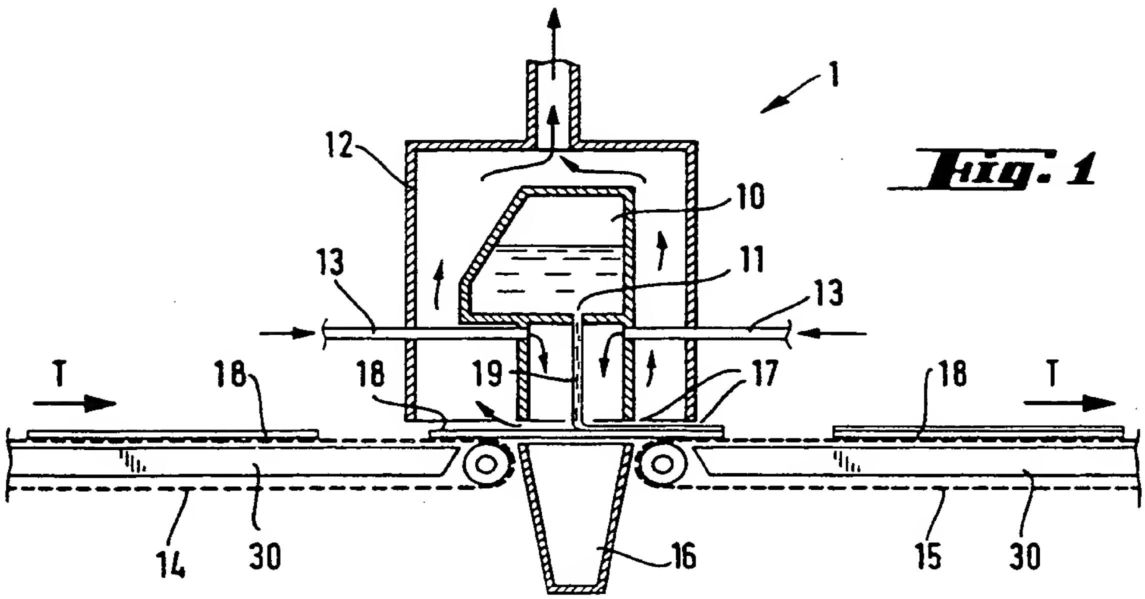
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Fig. 1

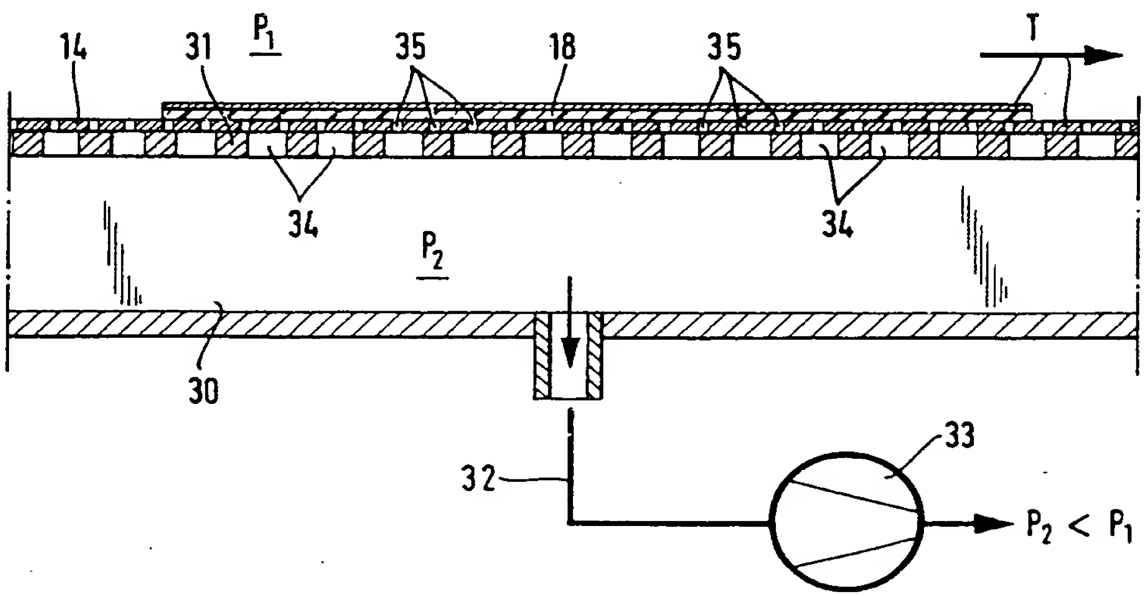
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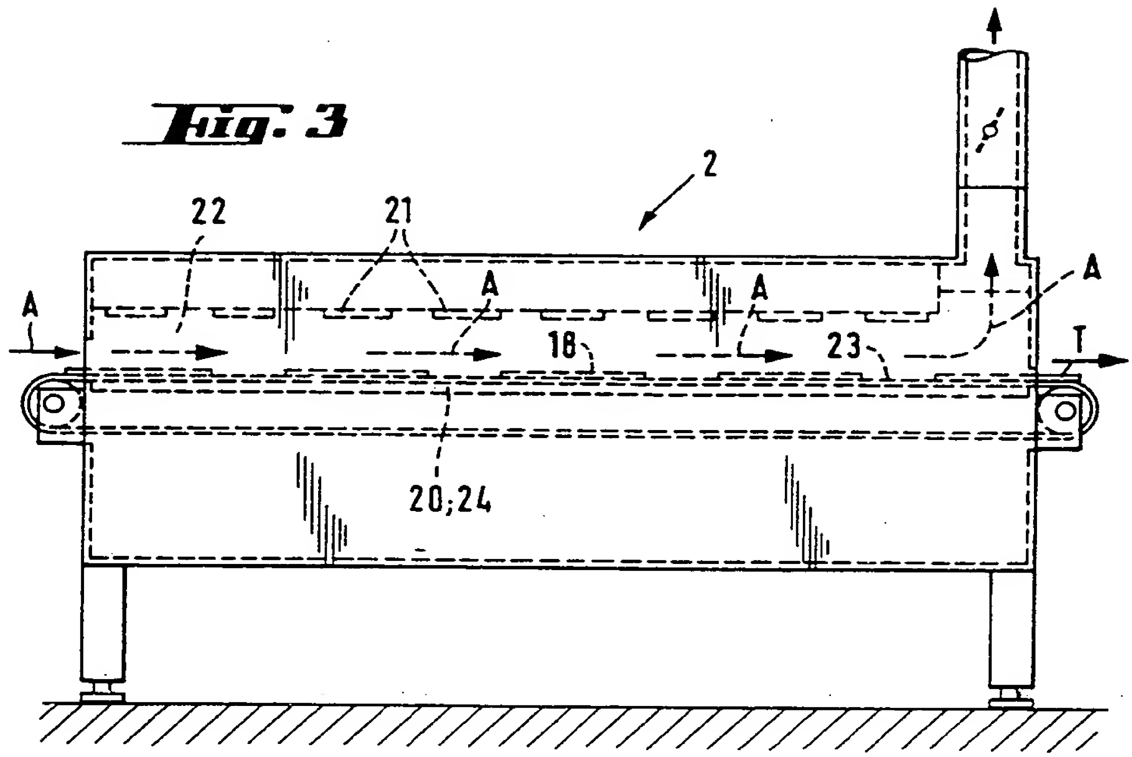
Fig. 2

Fig. 3



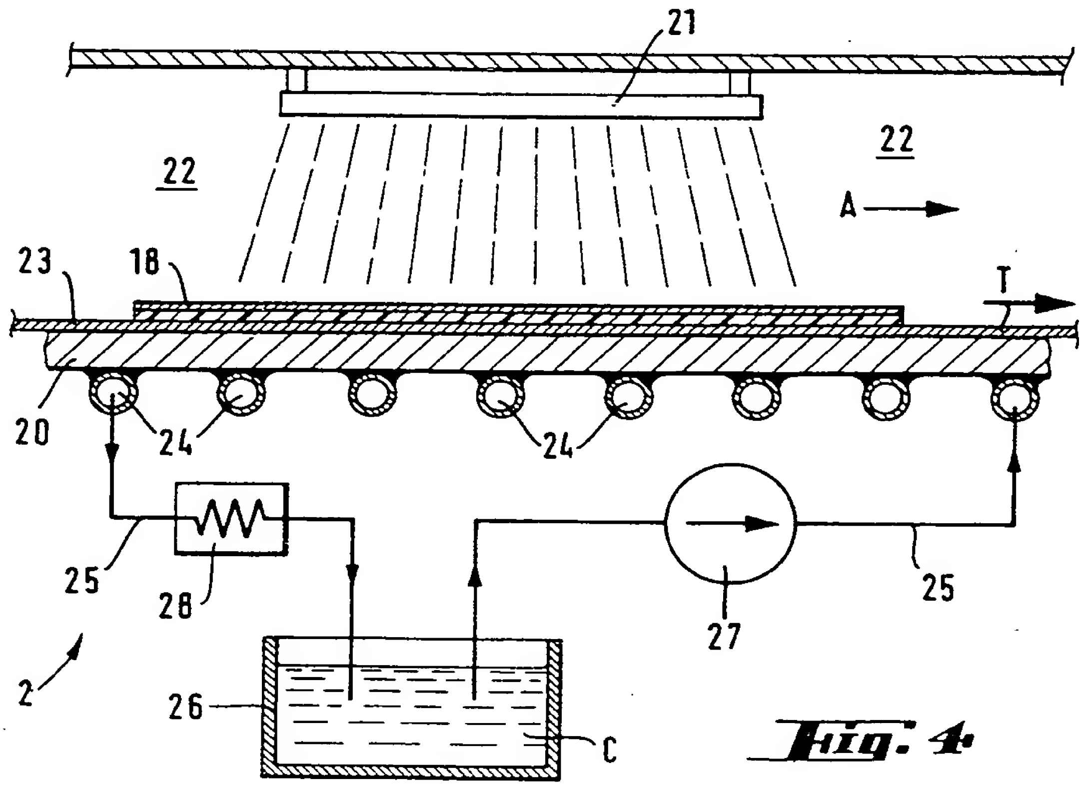


Fig. 4